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**Effect of Environmental Variables on Localized Corrosion
of High-Performance Container Materials**

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Abstract

The current high-level nuclear waste package design effort is focused on all-metallic multi- “ barrier concepts to accommodate the nation’s canistered and uncanistered spent nuclear fuels, and vitrified defense high-level waste canisters. This design incorporates a thick outer corrosion-allowance metal barrier over a thin inner container made of corrosion-resistant metal, so that the inner barrier may be galvanically protected if the outer barrier is breached. Electrochemical cyclic potentiodynamic polarization experiments were performed at the Lawrence Livermore National Laboratory (LLNL) on several candidate corrosion-resistant waste package container materials to evaluate their susceptibility to pitting corrosion in neutral, acidic, and alkaline brines containing 1, 5, and 10 weight percent NaCl at 90°C. The pH of these solutions ranged between 6 and 7, 2 and 3, and 10 and 11, respectively. Dynamic potential scans were done in the noble direction at rates of 0.043, 0.085, 0.17, and 0.34 mV/sec commencing at the stable corrosion potential, and continuing to a potential sufficiently noble to cause pitting prior to reversing the potential scan at the same rate. Materials tested include Fe-Ni-Cr-Mo Alloys 825, G-3, and G-3o; Ni-Cr-Mo Alloys C-4 and C-22; and titanium alloy Ti Gr-12.

Consistent with results of other investigators, the present study showed a shift in the critical pitting potential (E_{pit}) to more active (negative) values with increasing chloride ion(Cl^-) concentration. In the presence of chloride, the transition from passivity to pitting in susceptible alloys can be explained by a competitive adsorption mechanism by which Cl^- moves into the double layer (oxide/liquid interface). The alloy eventually reaches a critical potential, E_{pit} , corresponding to the Cl^- required to displace the adsorbed oxygen species. As to the effect of pH, E_{pit} was significantly shifted to more noble (positive) values with a change in pH from acidic to neutral. The more active E_{pit} value in acidic solution is the result of acceleration of the cathodic reaction due to the high concentration of hydrogen ion (H^+). At alkaline pH, except for Alloy 825, E_{pit} values were slightly lower compared to those in neutral solution. The fact that E_{pit} was shifted to more noble values (compared to those in acidic solutions) is consistent with the well-established pitting inhibition effect of hydroxyl ions. No consistent pattern on the effect of Cl^- and pH on the protection or repassivation potential was observed.

With respect to the effect of potential scan rate on E_{pit} , a general trend was not observed. In some cases, increasing the scan rate caused E_{pit} to become more noble. In other cases, the opposite behavior occurred. The overall results suggest that the desired localized corrosion resistance of the inner containment barrier may be achieved through use of materials such as Alloys C-4 and C-22, and Ti Gr- 12.

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